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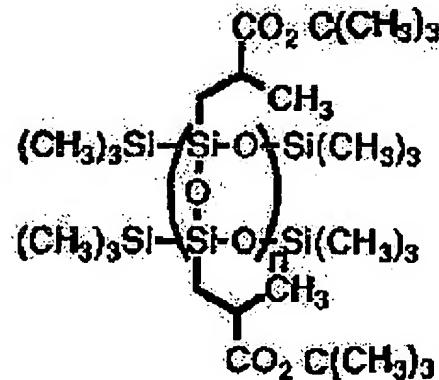
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(54) RADIATION SENSITIVE RESIN COMPOSITION

(57) Abstract:

PURPOSE: To obtain a novel radiation sensitive resin compsn. having high sensitivity and resolving power to radiation and excellent resistance to reactive ion etching with O₂.

CONSTITUTION: This radiation sensitive resin compsn. is a mixture of 0.5g t-butyl ester siloxane represented by the formula and having 137,900wt. average mol.wt. and 1.8 specific dispersion with 50mg triphenylsulfonium trifluoromethanesulfonate and 4ml 2-ethyl methoxyacetate as a solvent.



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CLAIMS

[Claim(s)]

[Claim 1] The radiation sensitivity resin constituent characterized by being Pori (siloxane), separating one or more carbon radicals to the side chain, and including Pori (siloxane) which has C-O association cut from an acid, and the acid generator which decomposes according to an operation of the radiation irradiated and generates an acid.

[Claim 2] The radiation sensitivity resin constituent according to claim 1 characterized by having C-O association of ester for Pori (siloxane) in the side chain.

[Claim 3] The radiation sensitivity resin constituent according to claim 1 characterized by having C-O association of phenol alkyl ether for Pori (siloxane) in the side chain.

[Claim 4] The radiation sensitivity resin constituent according to claim 1 characterized by having C-O association of alkyl ether for Pori (siloxane) in the side chain.

[Claim 5] The radiation sensitivity resin constituent according to claim 1 characterized by having used the acid generator as sulfonium salt and considering as 0.01 - 50% to the weight

of Pori (siloxane) using the addition.

[Claim 6] The radiation sensitivity resin constituent according to claim 1 characterized by having used the acid generator as iodonium salt and considering as 0.01 - 50% to the weight of Pori (siloxane) using the addition.

[Claim 7] The radiation sensitivity resin constituent according to claim 1 characterized by having used the acid generator as the aromatic compound which has at least one TORIKURORO methyl group, and considering as 0.01 - 50% to the weight of Pori (siloxane) using the addition.

[Claim 8] The radiation sensitivity resin constituent according to claim 1 characterized by having made the acid generator into p-toluene sulfonate and considering as 0.01 - 50% to the weight of Pori (siloxane) using the addition.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is usable as a component of a resist used by manufacture of a semiconductor device etc., and relates to the new radiation sensitivity resin constituent which induces radiations, such as light, an electron beam, an X-ray, or an ion beam.

[0002]

[Description of the Prior Art] The processing technique of submicron order is needed with high integration of LSI. Therefore, for example, at the etching process in LSI manufacture, the dry etching technique in which processing highly precise and detailed moreover is possible is adopted.

[0003] Here, a dry etching technique is a technique which etches the part which covered the

substrate which should be processed by the resist, carried out patterning of this resist using light, an electron ray, etc., and has been exposed from the mask of a substrate by the reactant gas plasma by using the obtained pattern as a mask. Therefore, the resist used with a dry etching technique consists of ingredients which have the resolution of submicron order, and sufficient reactant gas plasma resistance.

[0004] However, since the level difference of a processed substrate becomes still larger with high integration of LSI, the thickness of a resist layer is in the inclination thickened so that flattening of the above-mentioned level difference can be attained, and so that a resist may remain as a mask till substrate processing termination. Therefore, when are based on optical exposure and based on the constraint by the depth of focus of exposure optical system, and electron beam lithography, the constraint which comes from the scattering phenomenon of the electron in a resist is received, and in having used only the single resist layer, it is becoming difficult to etch a substrate minutely with high degree of accuracy. Then, a new resist process is examined variously and the bilayer resist process attracts attention as one of them.

[0005] This bilayer resist process is an approach using the layered product which consists of the thick polymer layer (polyimide and the layer of a photoresist which carried out heat curing are usually used.) for carrying out flattening of the substrate level difference, and the thin photoresist layer which is formed on it and has O₂-RIE resistance as a mask at the time of substrate etching. High resolving power is secured by the thin resist layer which is the upper resist, and the dry etching resistance at the time of substrate processing is secured by the lower layer resist.

[0006] As a component of the upper resist used for this bilayer resist process, the silicon content polymer with O₂-RIE resistance higher than a lower layer is suitable. Photoresist silicone resin is one of the typical thing. This is what blended the photoinitiator cross linking reagent or the photopolymerization initiator with the silicone resin used as a binder, and can be used as negative resist.

[0007] There were some which are indicated by JP,61-20030,A as an example of such photoresist silicone resin. This consists of the resin and bis-azide which have a double bond like Pori (acryloyloxy methylphenylethyl silsesquioxane), and has been used as high sensitivity negative resist for ultraviolet rays under nitrogen-gas-atmosphere mind.

[0008] There were some which are indicated by JP,60-49647,B as an example of further others. It is the thing of the system using polysilane as a photopolymerization initiator. It is shown that the constituent of the Pori (ORGANO siloxane) and the dodeca methyl cyclohexa silane which have a double bond specifically has a property good as ultraviolet-rays hardening resin.

[0009] There were some which are indicated by JP,55-127023,A as an example of further others. This is the thing of the system which uses organic peroxide as a photopolymerization

initiator. It is shown to this official report by by using a thing like various organic peroxide, for example, peroxy ester, with Pori (ORGANO siloxane) which has a double bond that a uniform hardening coat is obtained by UV irradiation.

[0010] Moreover, there were some by which consider as a thing completely different from what was described until now, for example, JP,61-144639,A is carried out. This is Pori (phenyl silsesquioxane) and cis- to a general-purpose positive type photoresist like OFPR-800 (TOKYO OHKA KOGYO CO., LTD. make). - (1, 3, 5, 7-tetra-hydroxy) Little addition of -1, 3 and 5, and the 7-tetra-phenyl cyclotetrasiloxane was carried out. According to this, it is a positive resist for the bilayer resist methods, and the resist in which the development by lye is possible was obtained.

[0011] Moreover, using things other than Pori (siloxane) as a binder is also examined. For example, it is indicated by JP,61-198151,A that the object using the novolak resin which has a trialkylsilyl group as a diazo naphthoquinone sensitization agent becomes the upper resist which has sensibility in the light.

[0012]

[Problem(s) to be Solved by the Invention] However, each conventional resist (photopolymer constituent) had the trouble that it explained below.

[0013] First, since the photo-curing reaction which intervenes and progresses an organic radical is generally checked by oxygen, if exposure of the thing of the photopolymer constituent using this kind of reaction, for example, JP,61-20030,A, is not performed by nitrogen-gas-atmosphere mind so that this official report may see, it cannot realize high sensitivity. Since this said also about the object of the indication to JP,55-127023,A, although the improvement in a property of the hardening film was found, by this object, hardening had the fault of requiring long duration. Moreover, according to the knowledge of the artificer of this application, although it is not the case where bis-azide is used for JP,60-49647,B also about the object of an indication, it turns out that it is difficult to realize sensibility high enough for the existence of oxygen.

[0014] On the other hand, by the object of the indication to JP,61-144639,A, since the addition of a silicon compound was not able to be made [many / so], and since the silicon content in the binder used for JP,61-198151,A by the object of an indication was low, there was a trouble that neither showed sufficient O₂-RIE resistance. Moreover, although the constituent concerned is made to constitute from the same idea as the general-purpose positive type photoresist which is excellent in micro-processing nature in both [these] the photopolymer constituent, since the polysiloxane is added by the object of an indication to JP,61-144639,A, and since silicon content novolak resin is used for JP,61-198151,A by the object of an indication, it is difficult to maintain the dissolution rate difference over the developer of the exposure section and the unexposed part which are realized by the general-purpose positive

type photoresist as it is.

[0015] For this reason, a resist pattern becomes thin at the time of etching which cannot make the throughput of semiconductor device manufacture high, and each conventional photopolymer constituent cannot perform highly precise substrate processing, or had the fault that a high resolution was not obtained.

[0016] This invention is made in view of such a point, therefore the purpose of this invention is to offer the radiation sensitivity resin constituent which has the O2-RIE resistance which has high sensibility and resolution and was excellent to the radiation.

[0017]

[The means for solving a technical problem and an operation] In order to aim at achievement of this purpose, according to the radiation sensitivity resin constituent (it may be hereafter called a "constituent" for short) of this invention It is characterized by including Pori (siloxane) as the 1st component which has C-O association which is Pori (siloxane), separates one or more carbon radicals to the side chain, and may be decomposed into it from an acid, and the acid generator as the 2nd component which decomposes according to an operation of the radiation irradiated and generates an acid.

[0018] According to the constituent of this invention, if radiations, such as light, an electron beam, an X-ray, or an ion beam, are irradiated alternatively at this, since the acid generator of a radiation irradiation part will generate an acid and this acid will act on C-O association of the side chain of Pori (siloxane) of this radiation irradiation part further, this C-O association is decomposed. Although condensation will occur and it will function as a constituent of a negative mold in Pori (siloxane) which C-O association which may be decomposed into Si of Pori (siloxane) from an acid couples directly by the oxygen side here (that is, it has structure of Si-O-C) if an operation of an acid attains to this Since Pori (siloxane) included in the constituent of this invention separates one or more carbon radicals to a side chain and it has the C-O association concerned, in that radiation irradiation part, a polar change produces condensation, without happening. therefore, a dissolution rate difference [as opposed to / since a difference polar in the radiation irradiation part (henceforth the "exposure section") and the non-irradiating part (henceforth an "unexposed part") of a constituent of this invention arises / the developer of both parts] -- being generated -- thereby -- high -- pattern formation [****] becomes possible. Moreover, since the polar difference between the exposure section and an unexposed part is used in this way, it can perform dissolving only the exposure section of the constituent after the alternative exposure of a radiation with a developer (using it as a resist of a positive type), or dissolving only an unexposed part with a developer (using it as a resist of a negative mold) to arbitration by choosing the class of developer.

[0019] Moreover, with the light exposure which the light exposure at the time of exposing the radiation sensitivity resin constituent concerned may make generate a desired (the amount of

catalysts) acid from an acid generator, since a polar change in Pori (siloxane) as the 1st component is produced in few acids from the acid generator as the 2nd component acting, since it will be good, the constituent concerned will become high sensitivity.

[0020] Moreover, since Pori (siloxane) as the 1st component has silicon-oxygen association in the principal chain and it is efficiently changed into a silicon dioxide in process of processing by the oxygen plasma, dry etching resistance is also secured.

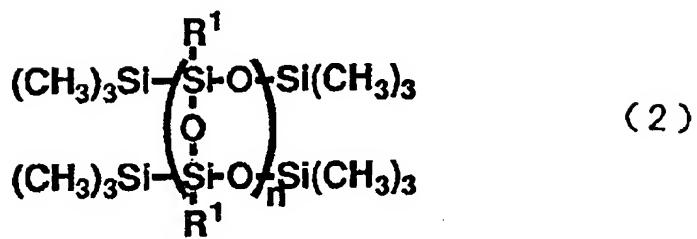
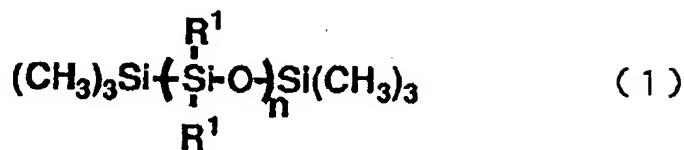
[0021] Here, as an example of Pori (siloxane) as the 1st component, Pori (siloxane) which has C-O association of alkyl ether can be mentioned to Pori (siloxane) which has C-O association of ester in a side chain, Pori (siloxane) which has C-O association of phenol alkyl ether in a side chain, and a side chain, for example.

[0022] Each Pori (siloxane) shown in a side chain as an example of Pori (siloxane) of having C-O association of ester, by (1), (2), (following 3), or following (4) types, for example can be mentioned. However, n in a formula is polymerization degree and R1. As [show / are ester which may be decomposed from an acid, for example, / by the following (a) type] Moreover, R2 It is an acidolysis nature protective group, for example, they are the 3rd alkyl group, for example, alpha-permutation benzyl as shown by following (d) or (e) formula, for example, a diphenyl ethyl group as shown by the following (f) formula, as shown by following (b) or (c) formula, for example, alpha-permutation cyclo propyl group as shown by the following (g) formula, or a permutation cyclohexenyl group as shown by the following (h) formula

[0023] When using for a side chain Pori (siloxane) which has C-O association of ester as Pori (siloxane) which is the 1st component, this side chain will become a carboxylic acid if the acid from an acid generator acts. Since ester is the typical oleophilic matter and one carboxylic acid is the typical hydrophilic matter, a difference polar by the exposure section and the unexposed part arises: For this reason, since the soluble difference to a developer will be obtained, pattern formation becomes possible. Moreover, since the acidity of a carboxylic acid is stronger than a phenol, it can make polar change of the exposure section larger than the case where the two below-mentioned persons' Pori (siloxane) is used. For this reason, when raising resolution compared with the two below-mentioned persons, it is still much more advantageous. Moreover, both an alkali developer and an organic solvent can be used as a developer.

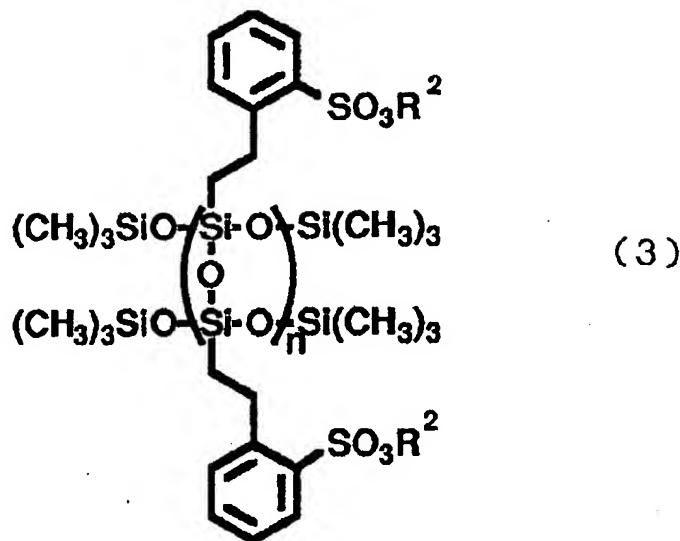
[0024]

[Formula 1]

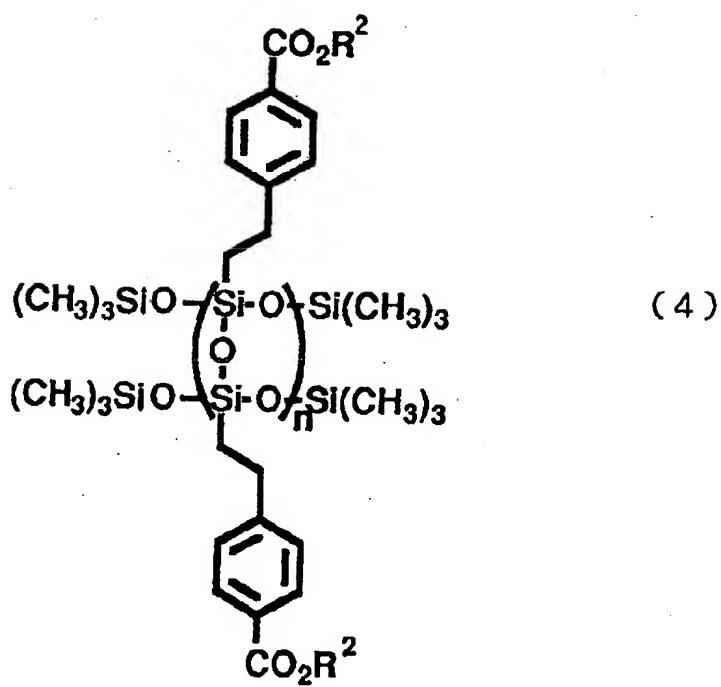


[0025]

[Formula 2]



(3)



(4)

[0026]

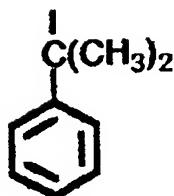
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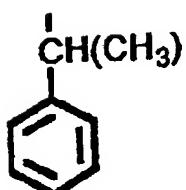
(b)



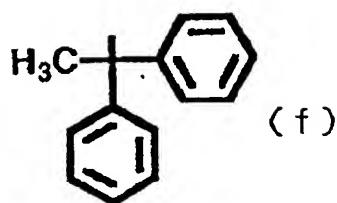
(c)



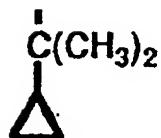
(d)



(e)



(f)



(g)



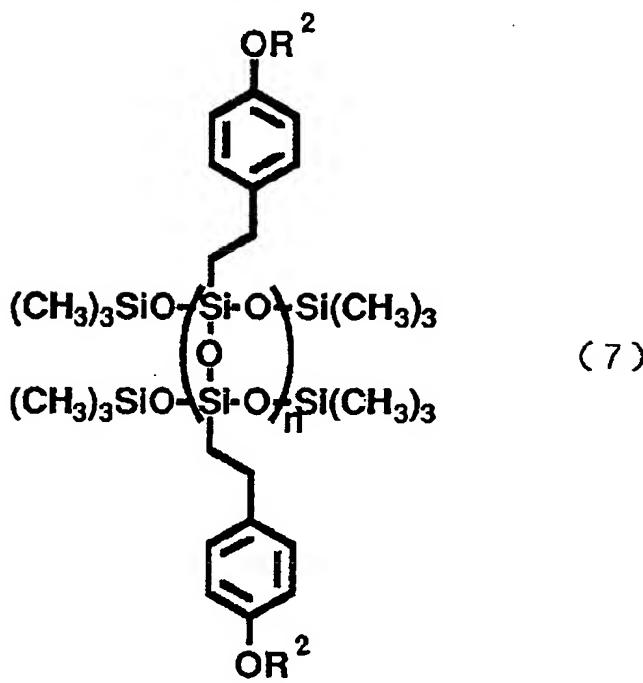
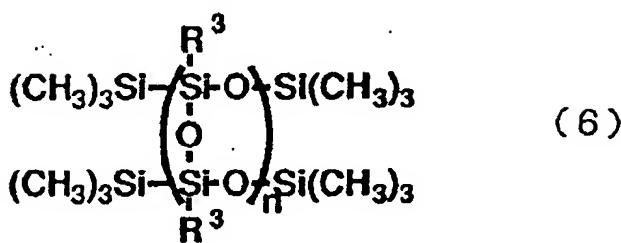
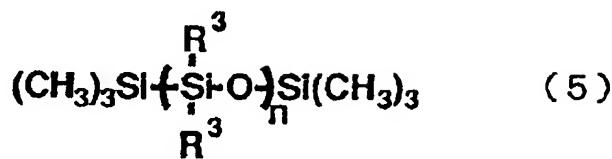
(h)

[0027] Moreover, what is shown in a side chain by (5), (following 6), or following (7) formula, for example as an example of Pori (siloxane) of having C-O association of phenol alkyl ether can be mentioned. However, the inside n of a formula is polymerization degree and R3. As [show / are phenol ether which may be disassembled from an acid, for example, / by the following (i) type] Moreover, R2 It is like [it is an acidolysis nature protective group, for example,] above-mentioned (a) - (h). When using for a side chain Pori (siloxane) which has C-

O association of phenol alkyl ether as Pori (siloxane) which is the 1st component, this side chain will become a phenol if the acid from an acid generator acts. Since the ether is the typical oleophilic matter and one phenol is the typical hydrophilic matter, a difference polar by the exposure section and the unexposed part arises. For this reason, since the soluble difference to a developer will be obtained, pattern formation becomes possible. Also in this case, both an alkali developer and an organic solvent can be used as a developer.

[0028]

[Formula 4]

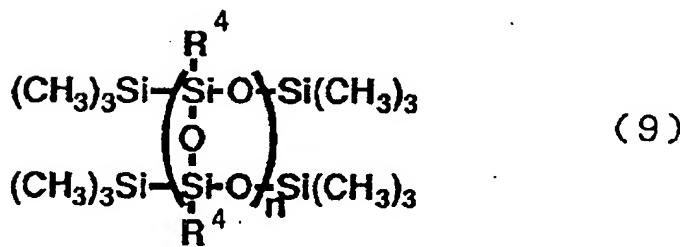
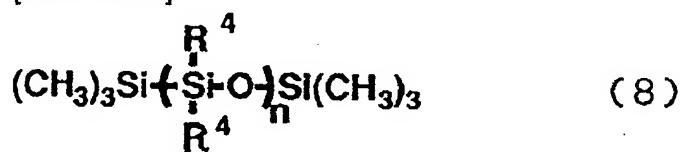


[0029] Moreover, what is shown in a side chain by (following 8) or following (9) formula as an example of Pori (siloxane) of having C-O association of alkyl ether, for example can be mentioned. However, the inside n of a formula is polymerization degree and R4. As [show /

are alkyl ether which may be decomposed from an acid, for example, / by the following (j) type] Moreover, R₂ It is like [it is an acidolysis nature protective group, for example,] above-mentioned (a) - (h). Also when using for a side chain Pori (siloxane) which has C-O association of alkyl ether as Pori (siloxane) which is the 1st component, a difference arises in the polarity of the exposure section and an unexposed part in the same reason as the case where Pori (siloxane) which has C-O association of phenol alkyl ether is used for a side chain. For this reason, since the soluble difference to a developer will be obtained, pattern formation becomes possible. However, although development by the alkali developer cannot be performed in this case, negatives can be developed with an organic solvent.

[0030]

[Formula 5]

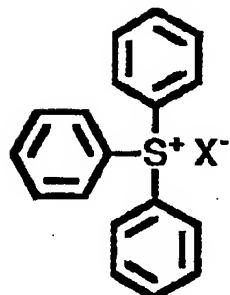


[0031] In addition, the suitable molecular weight range of Pori (siloxane) which is the 1st component can be chosen as arbitration according to the spreading nature to the substrate of the radiation sensitivity resin constituent concerned etc. If it is the case where the radiation sensitivity resin constituent concerned is used as a resist, since it is required that filtration with a filter is meltable [to a solvent] for that formation of a solid-state film is possible and resist spreading solution preparation and easy, to obtain desired resolution, etc., the molecular weight is good to consider as the range of 1000-1 million.

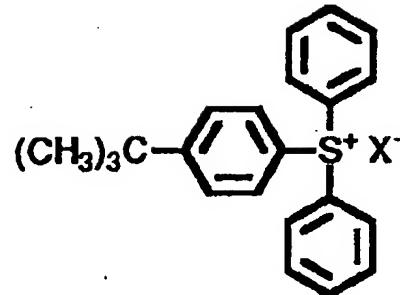
[0032] Moreover, the various things known from the former can be used for the acid generator which is the 2nd component of the radiation sensitivity resin constituent of this invention. However, since the catalysis is weak, halide acid is seldom suitable. For example, since various kinds of p-toluene sulfonates shown by various kinds of aromatic compounds which have at least one TORIKURORO methyl group shown by various kinds of iodonium salt, following formulas (V), and formulas (VI) which are shown by various kinds of sulfonium salt, following formulas (III), and formulas (IV) which are shown by a following formula (I) and a following formula (II), and the following formula (VII) generate an acid stronger than halide acid, they are suitable.

[0033]

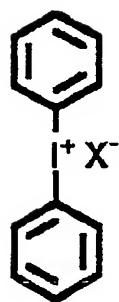
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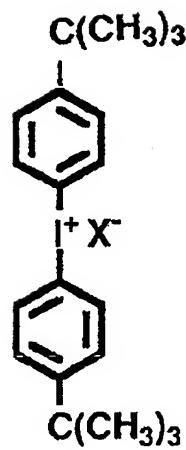
(I)



(II)



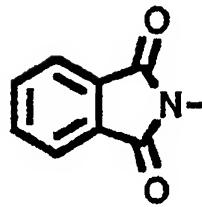
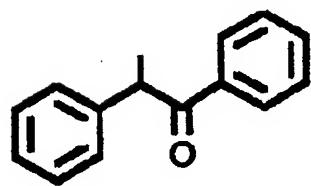
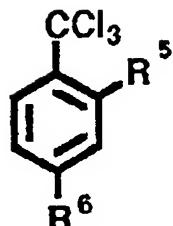
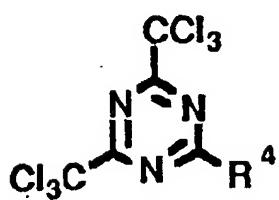
(III)



(IV)

[0034]

[Formula 7]



[0035] however, X- in a formula (I) - a formula (IV) for example, B4-, AsF6-, SbF6-, ClO4-, or CF3SO3- expressing -- R4 in a formula (V) for example, the radical shown by CCl3 or the above-mentioned formula (A), (B), (C), (D), or (E) -- expressing -- R5 in a formula (VI) for example, Cl or H -- it is -- R6 [and] For example, Cl or CCl3 it is -- R7 [moreover,] in a

formula (VII) For example, the radical shown by an above-mentioned formula (F) or an above-mentioned formula (G) is expressed.

[0036] An above-mentioned acid generator is approach [journal OBU polymer Science are marketed or according for example, to Jay buoy Crivello (J. V.Crivello) etc., and a polymer chemistry edition (J. it is compoundable with Polymer Sci., Polymer Chem.Ed., 18, and 2677 (1980)].).

[0037] It is good 0.01 - 50% of the weight of the range, and to add these acid generators preferably to the weight of Pori (siloxane) to be used in the amount of 0.05 - 30% of the weight of the range. It is because the sensibility of the radiation sensitivity resin constituent concerned will be low or that spreading film will become brittle, if it separates from this range.

[0038] Moreover, when applying the constituent concerned on a substrate with a spin coat method in use of this radiation sensitivity resin constituent and forming this coat on a substrate, the solvent for spreading solution preparation for it is needed. As this solvent, for example, 2-methoxy ethyl acetate, methyl isobutyl ketone (MIBK), a cellosolve acetate, methyl-cellosolve acetate, dioxane, etc. can be mentioned.

[0039] Moreover, in use of this radiation sensitivity resin constituent, enhancement of an operation of the acid generator in a radiation irradiation part can be urged to the coat of the constituent concerned by heat-treating this sample after irradiating a radiation.

[0040]

[Example] Hereafter, the example of the radiation sensitivity resin constituent of this invention is explained. In addition, numerical conditions, such as the material of construction which the following explains and is mentioned and its amount, the processing time, processing temperature, and thickness, are only the suitable examples of this invention within the limits. Therefore, this invention is not limited only to these conditions. Moreover, each example described below is an example which uses Pori (siloxane) which has C-O association which separates three or more carbon radicals to the side chain, and may be decomposed into it from an acid as Pori (siloxane).

[0041] <The 1st - the 5th example> The example using Pori (siloxane) which has C-O association of ester in a side chain is first explained as the 1st - the 5th example, respectively.

[0042] 1. Use t-butyl ester siloxane (R1 in the above-mentioned (2) types is the above-mentioned (a) formula, and R2 in the (a) type is the thing of -C(CH₃)₃) as Pori (siloxane) which is the 1st component of the constituent of invention of the 1st *****. as the acid generator which is the 2nd component -- a triphenylsulfonium trifluoromethane sulfonate (the inside of a formula (I), and the thing whose X- is CF₃SO₃-) The used example (the 1st example) is explained.

[0043] According to the approach of J.L.Speier and others of an indication, t-butyl methacrylate is hydrosilylated as follows in hydrosilylation **** of the synthetic 1-1-1. t-butyl methacrylate of

a 1-1-t-butyl ester siloxane, and reference (J. Amer. Chem. Soc. and 79,974 (1957)).

[0044] Trimethoxysilane 48.8g is put into 4 opening flask equipped with an agitator, a reflux condenser, and a thermometer, and the nitrogen purge of the interior is carried out. After putting this into a water bath and cooling, 4ml of 2-propanol (IPA) solutions of 0.1 mol/l (liter) chloroauric acid is added into this flask. After stirring the thing in a flask for 15 minutes, a syringe is used for this and 13g of t-butyl methacrylate is dropped at it. After stirring for 30 minutes, mixture is heated at 80 degrees C. It cools, after stirring for 18 hours. After diluting mixture with a cyclohexane, it filters through cerite. If reduced pressure distilling off of the filtrate is carried out, 24g of orange oily matter will be obtained.

[0045] About this oily matter, an NMR (nuclear magnetic resonance) spectrum and IR (infrared rays) spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC (gel permeation chromatography). The result was as follows.

[0046] NMR;delta 3.2 (methoxyl group) and 1.05 (t-butyl), IR; wave number 2845cm⁻¹ (methoxyl group), 1730 (ester), 1194, 1147 and 1094 (methoxy silyl, siloxane), GPC;MW =91600, MW/Mn =13.8.

[0047] 1-1-2. As it is the following, change hydrolysis, condensation, next the above-mentioned orange oily matter into a ladder siloxane.

[0048] Water cooling of the 24g of the above-mentioned orange oily matter is dissolved and carried out to 1.2l. (liter) 4-methyl-2-butanone (MIBK). 50ml water and 1.2ml triethylamine are added to this, respectively. After stirring for 30 minutes, it heats in temperature of 80 degrees C, and is made to react for 18 hours. After diluting after [MIBK] cooling, next adding the hydrochloric acid of 1 mol/l (liter) to this and considering as acidity, this is washed with water until it becomes neutrality. Next, after washing with brine, an extract is dried with magnesium sulfate. If reduced pressure distilling off of the filtrate is carried out after filtering this, a 12g solid-state will be obtained.

[0049] About this solid-state, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0050] NMR;delta1.0 (t-butyl) and IR; wave number [of 1724cm] - 1 (ester), 1136 (siloxane), GPC;MW =89400, and MW/Mn =8.0.

[0051] 1-1-3. Protect the silanol of the end of Pori (siloxane) by the trimethylsilyl radical as follows for trimethylsilylation, next stabilization of a polymer. It is for preventing the condensation of Pori (siloxane) progressing by existence of a silanol. Here, it carries out to reference (539 Proc.SPIE, 70 (1985)) as follows by the approach of R.G.Brault and others of an indication.

[0052] The 12g of the above-mentioned solid-states is dissolved in a 300ml tetrahydrofuran (THF), trimethylchlorosilane 12g and triethylamine 12g are added to this solution one by one,

and it stirs at a room temperature for 18 hours. A reactant is filtered through cerite and reduced pressure distilling off of the filtrate is carried out. The residue is dissolved in toluene 200ml, and a solid-state will be obtained, if it filters through cerite again and reduced pressure distilling off of the filtrate is carried out. White precipitate will be obtained, if it is dropped into a 300ml cold methanol after dissolving this solid-state in 10ml toluene. This precipitate is carried out a ** exception and a vacuum drying is carried out at a room temperature 1 night. The resin of the 9.5g purpose is obtained.

[0053] About this resin, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0054] NMR;delta 1.0 (t-butyl) and 0.0 (trimethyl sill radical, very minute amount) and IR; wave number [of 1724cm] - 1 (ester), 1138 (siloxane), GPC;MW =137900, and MW/Mn =1.8.

[0055] 1-2. preparation of the constituent (resist solution) of the 1st example -- mix 4ml of 2-methoxy ethyl acetate with t-butyl ester siloxane (MW =137900, MW/Mn =1.8) 0.5g compounded as mentioned above and triphenylsulfonium trifluoromethane sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 1st example is prepared.

[0056] 1-3. Apply the resist solution of the 1st example prepared by example 1.2 term using a patterning experiment 1-3-1. alkali developer with a spin coat method on a silicon wafer. This SHIRIKO wafer is prebaked for 1 minute at the temperature of 80 degrees C using a hot plate, and the coat whose thickness of the constituent of the 1st example is 0.25 micrometers is formed on a SHIRIKO wafer. Next, electron-beam-lithography equipment (ELS3300 by Elionix, Inc.) is used for this sample, and the graphic form for evaluation is changed and considerable-number-drawn for light exposure on conditions with an acceleration voltage of 20kV. BEKU after exposure is carried out for a sample [finishing / exposure] for 2 minutes at the temperature of 120 degrees C using a hot plate. Next, this sample is developed for 1 minute in 1.0% (1g / 100ml) of tetramethylammonium hydroxide water solution, and a rinse is further carried out for 1 minute with pure water. In this case, the resist pattern by which the electron-beam-irradiation part of a coat was dissolved in the developer was obtained.

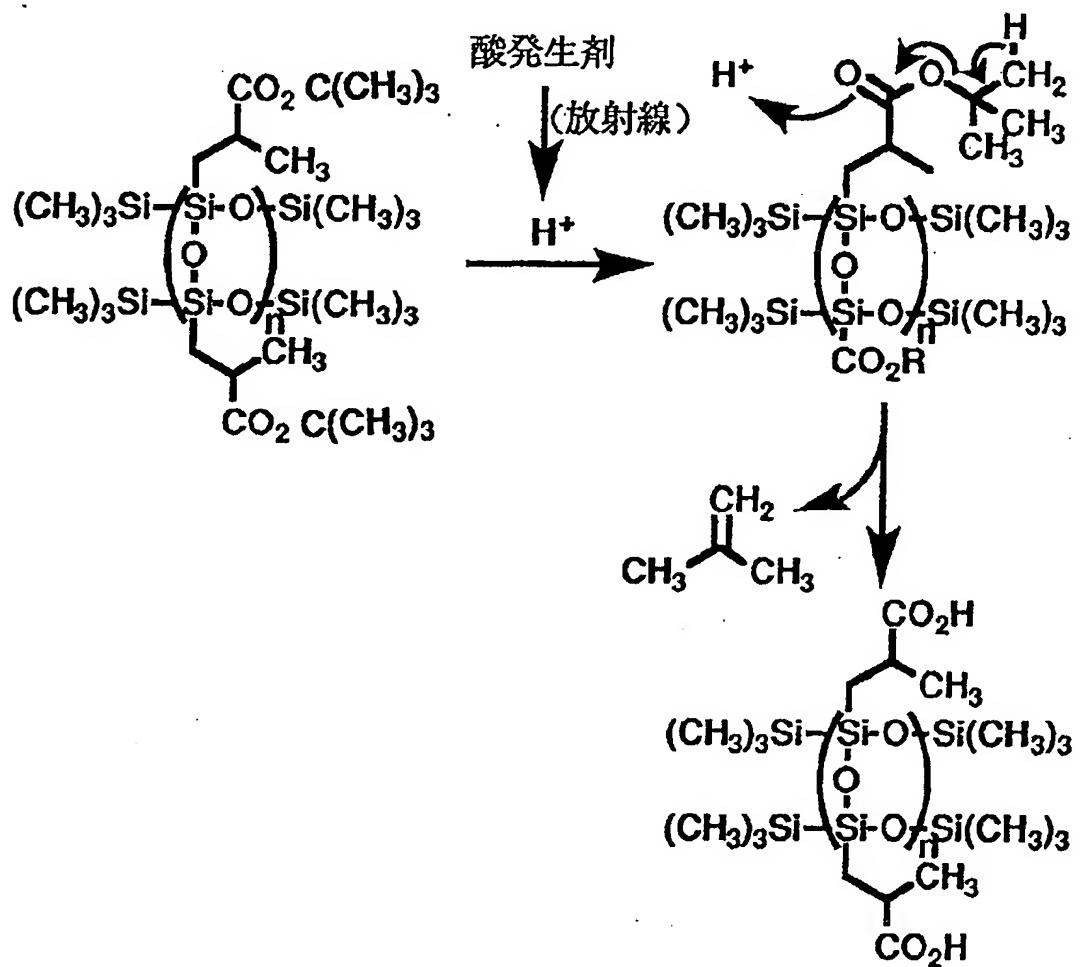
[0057] Next, the residual thickness after development is measured by TARISU tetraethylpyrophosphate (rank tailor HOBUSON film production thickness meter). The curvilinear ***** characteristic curve which plotted the value which standardized it by initial thickness to the logarithm of light exposure is created. the place which searched for sensibility and contrast by that cause -- respectively -- 1.5microC/cm² it is -- it was 5.2. Moreover, when this resist pattern was observed with the scanning electron microscope (SEM), it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0058] Signs that the ester of the side chain of t-butyl ester siloxane which is the 1st component of the constituent of the 1st example was changed into a carboxylic acid according

to an operation of the acid from an acid generator were shown in the following (10) types. t-butyl of the side chain of t-butyl ester siloxane is easily removed from an acid in catalyst, and ester is changed into a carboxylic acid. Although a polar change of Pori (siloxane) also produces the constituent of each following example by the same principle as the thing of this 1st example, the publication of that reaction formula is omitted in the 2nd example.

[0059]

[Formula 8]



(10)

[0060] 1-3-2. Make the **** developer for examples using the organic solvent as a developer into 2/1 (volume ratio) mixed liquor of a cyclohexane/dichloromethane, make developing time by this into 20 seconds, and conduct a patterning experiment in the procedure of a 1-3-1. term, and the same procedure except performing a rinse for 20 seconds by the cyclohexane. In this case, the resist pattern by which the electron ray non-irradiated part of a coat was dissolved in the developer was obtained. Moreover, in quest of sensibility and contrast, pattern observation is carried out in the procedure of a 1-3-1. term, and the same procedure. sensibility -- 2.5microC/cm² it is -- contrast was 5.0. Moreover, it turned out that 0.4-micrometer Rhine -

and - tooth space are resolved.

[0061] 1-4. Thickness forms the resist layer which is 2 micrometers and which carried out heat curing on a silicon wafer as a lower layer about O2-RIE resistance. Next, the resist solution of the 1st example is applied with a spin coat method on this lower layer. Next, this SHIRIKO wafer is prebaked for 1 minute at the temperature of 80 degrees C using a hot plate, and the thickness as the upper layer which consists of the constituent of the 1st example forms the coat which is 0.25 micrometers. Electron-beam-lithography equipment (ELS3300 by Elionix, Inc.) is used for this sample, and the graphic form for evaluation is changed and considerable-number-drawn for light exposure on conditions with an acceleration voltage of 20kV. BEKU after exposure is carried out for a sample [finishing / exposure] for 2 minutes at the temperature of 120 degrees C using a hot plate. Next, this sample is developed for 1 minute in 1.0% (1g / 100ml) of tetramethylammonium hydroxide water solution, and a rinse is further carried out for 1 minute with pure water.

[0062] Oxygen plasma etching of the obtained sample is carried out for 40 minutes using the dry etcher called DEM451 made from Japanese ** Anelva on oxygen gas flow rate 50sccm, RF power density 0.12 W/cm², and conditions with a gas pressure of 1.3Pa.

[0063] When this plasma-etching finishing sample was observed by SEM, it turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration. in addition, the light exposure for obtaining such a pattern -- 2.0microC/cm² it was .

[0064] Moreover, the developer used in the case of the upper patterning is made into 2/1 (volume ratio) mixed liquor of a cyclohexane/dichloromethane, developing time by this is made into 20 seconds, and an above-mentioned procedure and the same procedure perform patterning and oxygen plasma etching except performing a rinse for 20 seconds by the cyclohexane. It turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration like the case where an alkali developer is used also in this case. however, the light exposure for obtaining such a pattern -- 3.0microC/cm² it was .

[0065] 2. Make the 1st component of the constituent of invention of the 2nd ***** into the same Pori (siloxane) as the 1st example, and explain the example (the 2nd example) using the benzoin p-toluene sulfonate (the inside of a formula (VII), thing whose R6 is the (F) type.) as an acid generator which is the 2nd component.

[0066] 2-1. Mix 4ml of 2-methoxy ethyl acetate with preparation t-butyl ester siloxane (MW =137900, MW/Mn =1.8) 0.5g of the constituent (resist solution) of the 2nd example, and benzoin p-toluene sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 2nd example is prepared.

[0067] 2-2. Conduct the patterning experiment at the time of using an alkali developer (1% tetramethylammonium hydroxide water solution) to the constituent of this 2nd example according to the procedure explained by the 1-3-1. term of the 1st example of a patterning experiment. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 3.5microC/cm² it is -- contrast was 8.2. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved again.

[0068] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 2nd example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 5.8microC/cm² it is -- contrast was 9.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0069] 3. Explain the example (the 3rd example) using the triphenylsulfonium trifluoromethane sulfonate used in the 1st example as an acid generator which is the 2nd component, using Pori (t-butoxy cull BONIRUFENECHIRU siloxane) (R2 of (4) types being the thing of -C(CH₃)₃) as Pori (siloxane) which is the 1st component of the constituent of invention of the 3rd *****.

[0070] 3-1. Perform processing explained in the 1-1-1. term of the 1st example except using 4-t-butoxy cull BONIRUSUCHIREN 20.4g instead of 13g of t-butyl methacrylate in the procedure of hydrosilylation explained in hydrosilylation **** of synthetic 3-1-1.4-t-butoxy cull BONIRUSUCHIREN of Pori (t-butoxy cull BONIRUFENECHIRU siloxane), and the 1-1-1. term of the 1st example. Thereby, 28g of orange oily matter is obtained.

[0071] About this oily matter, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0072] NMR;delta 7.5, 8.2 (aromatic series proton), 3.3 (methoxyl group) and 1.06 (t-butyl), IR; wave number 2845cm⁻¹ (methoxyl group), 1720 (ester), 1194, 1147 and 1094 (methoxy silyl, siloxane), GPC;MW =5600, MW/Mn =8.7.

[0073] 3-1-2. Change into a ladder siloxane according to hydrolysis, condensation, next the procedure that explained the 28g of the above-mentioned orange oily matter in the 1-1-2. term of the 1st example. Thereby, a 19g solid-state is obtained.

[0074] About this solid-state, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0075] NMR;delta 1.0 (t-butyl) and IR; wave number [of 1720cm] - 1 (ester), 1120 (siloxane), GPC;MW =7500, and MW/Mn =8.5.

[0076] 3-1-3. Perform processing for protecting the silanol of the end of Pori (siloxane) by the trimethylsilyl radical according to the procedure explained by trimethylsilylation, next the 1-1-3.

term of the 1st example for stabilization of a polymer. Namely, the 19g of the above-mentioned solid-states is dissolved in a 300ml tetrahydrofuran (THF), trimethylchlorosilane 12g and triethylamine 12g are added to this solution one by one, and it stirs at a room temperature for 18 hours. A reactant is filtered through cerite and reduced pressure distilling off of the filtrate is carried out. The residue is dissolved in toluene 200ml, it filters through cerite again, reduced pressure distilling off of the filtrate is carried out, and a solid-state is obtained. After dissolving this solid-state in 20ml toluene in this case, it is dropped into a 300ml cold methanol, and white precipitate is obtained. This precipitate is carried out a ** exception and a vacuum drying is carried out at a room temperature 1 night. The resin of the 16.5g purpose is obtained.

[0077] About this resin, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0078] NMR;delta 1.0 (t-butyl) and 0.0 (trimethyl sill radical, very minute amount) and IR; wave number [of 1720cm] - 1 (ester), 1120 (siloxane), GPC;MW =7900, and MW/Mn =1.5.

[0079] 3-2. preparation of the constituent (resist solution) of the 3rd example -- mix 4ml of 2-methoxy ethyl acetate with Pori (t-butoxy cull BONIRUFENECHIRU siloxane) (MW =7900, MW/Mn =1.5) 0.5g compounded as mentioned above and triphenylsulfonium trifluoromethane sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 3rd example is prepared.

[0080] 3-3. Conduct the patterning experiment at the time of using an alkali developer (1% tetramethylammonium hydroxide water solution) to the constituent of this 3rd example according to the procedure explained by the 1-3-1. term of the 1st example of a patterning experiment. And sensibility, contrast, and resolution are investigated, respectively.

consequently, sensibility -- 2.5microC/cm² it is -- contrast was 6.5. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved again.

[0081] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 3rd example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 4.5microC/cm² it is -- contrast was 7.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0082] 3-4. Form the pattern of the constituent of the 3rd example on a lower layer with the procedure explained in the 1-4. term of the 1st example about O2-RIE resistance, and the same procedure, and carry out oxygen plasma etching to this sample further.

[0083] When this plasma-etching finishing sample was observed by SEM, it turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration. in addition, the light exposure for obtaining such a pattern -- 7.0microC/cm² it was .

[0084] Moreover, the developer used in the case of the upper patterning is made into 2/1 (volume ratio) mixed liquor of a cyclohexane/dichloromethane, developing time by this is made into 20 seconds, and an above-mentioned procedure and the same procedure perform patterning and oxygen plasma etching except performing a rinse for 20 seconds by the cyclohexane. It turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration like the case where an alkali developer is used also in this case. however, the light exposure for obtaining such a pattern -- 8.0microC/cm² it was .

[0085] 4. Make the 1st component of the constituent of invention of the 4th ***** into the same Pori (siloxane) as the 3rd example, and explain the example (the 4th example) using the benzoin p-toluene sulfonate used in the 2nd example as an acid generator which is the 2nd component.

[0086] 4-1. Mix 4ml of 2-methoxy ethyl acetate with preparation Pori (t-butoxy cull BONIRUFENECHIRU siloxane) (MW =7900, MW/Mn =1.5) 0.5g of the constituent (resist solution) of the 4th example, and benzoin p-toluene sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 2nd example is prepared.

[0087] 4-2. Conduct the patterning experiment at the time of using an alkali developer (1% tetramethylammonium hydroxide water solution) to the constituent of this 4th example according to the procedure explained by the 1-3-1. term of the 1st example of a patterning experiment. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 5.5microC/cm² it is -- contrast was 8.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0088] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 4th example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 6.8microC/cm² it is -- contrast was 9.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0089] 5. Explain the example (the 5th example) using the triphenylsulfonium trifluoromethane sulfonate used in the 1st example as an acid generator which is the 2nd component, using a sulfonic-acid t-butyl ester siloxane (the (3) type R₂ being the thing of -C(CH₃)₃.) as Pori (siloxane) which is the 1st component of the constituent of invention of the 5th *****.

[0090] 5-1. Perform processing explained in the 1-1-1. term of the 1st example except using 4-t-butoxy sulfonyl styrene 24g instead of 13g of t-butyl methacrylate in the procedure of hydrosilylation explained in hydrosilylation **** of the synthetic 5-1-1.2-t-butoxy sulfonyl styrene of a sulfonic-acid t-butyl ester siloxane, and the 1-1-1. term of the 1st example. Thereby, 30g

of orange oily matter is obtained.

[0091] About this oily matter, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0092] NMR;delta 7.5-7.8 (aromatic series proton), 3.5 (methoxyl group) and 1.15 (t-butyl), IR; wave number 2845cm⁻¹ (methoxyl group), 1350 (sulfonate), 1194, 1147 and 1094 (methoxy silyl, siloxane), GPC;MW =1200, MW/Mn =1.6.

[0093] 5-1-2. Change into a ladder siloxane according to hydrolysis, condensation, next the procedure that explained the 30g of the above-mentioned orange oily matter in the 1-1-2. term of the 1st example. Thereby, a 15g solid-state is obtained.

[0094] About this solid-state, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0095] NMR;delta 7.5-7.8 (aromatic series proton), 1.15 (t-butyl), and IR; wave number [of 1350cm] - 1 (sulfonate), 1120 (siloxane), GPC;MW =4200, and MW/Mn =5.5.

[0096] 5-1-3. Perform processing for protecting the silanol of the end of Pori (siloxane) by the trimethylsilyl radical according to the procedure explained by trimethylsilylation, next the 3-1-3. term of the 3rd example for stabilization of a polymer to the 15g of the above-mentioned solid-states. Thereby, the resin of the 13.5g purpose is obtained.

[0097] About this resin, an NMR spectrum and IR SUPEKUTO are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0098] NMR;delta 7.5-7.8 (aromatic series proton), 1.15 (t-butyl) and 0.0 (trimethyl sill radical, very minute amount), and IR; wave number [of 1350cm] - 1 (sulfonate), 1120 (siloxane), GPC;MW =4300, and MW/Mn =2.5.

[0099] 5-2. preparation of the constituent (resist solution) of the 5th example -- mix 4ml of 2-methoxy ethyl acetate with sulfonic-acid t-butyl ester siloxane (MW =4300, MW/Mn =2.5) 0.5g compounded as mentioned above and triphenylsulfonium trifluoromethane sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 5th example is prepared.

[0100] 5-3. Conduct the patterning experiment at the time of using an alkali developer (however, 0.8% tetramethylammonium hydroxide water solution) to the constituent of this 5th example according to the procedure explained by the 1-3-1. term of the 1st example of a patterning experiment. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 1.2microC/cm² it is -- contrast was 2.0. Moreover, it turned out that 0.5-micrometer Rhine - and - tooth space are resolved again.

[0101] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 5th

example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 3.5microC/cm² it is -- contrast was 3.5. Moreover, it turned out that 0.5-micrometer Rhine - and - tooth space are resolved.

[0102] 5-4. Form the pattern of the constituent of the 5th example on a lower layer with the procedure explained in the 1-4. term of the 1st example about O₂-RIE resistance, and the same procedure, and carry out oxygen plasma etching to this sample further. However, the developer uses the tetramethylammonium hydroxide water solution 0.8%.

[0103] When this plasma-etching finishing sample was observed by SEM, it turned out that Rhine - and - tooth-space pattern which are 0.5 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration. in addition, the light exposure for obtaining such a pattern -- 2.5microC/cm² it was .

[0104] 6. Explain the example using Pori (siloxane) which has C-O association of phenol alkyl ether in a side chain as the 6th example, next the 6th example as Pori (siloxane) which is the 1st component. At this 6th example, it is R₂ of the above-mentioned (7) formula as such Pori (siloxane). Pori (siloxane) which is -C(CH₃) is used.

[0105] 6-1. Perform processing explained in the 1-1-1. term of the 1st example except using 4-t-butoxy styrene 17.6g instead of 13g of t-butyl methacrylate in the procedure of hydrosilylation explained in hydrosilylation **** of the synthetic 6-1-1.4-t-butoxy styrene of t-butyl ether siloxane of a phenol, and the 1-1-1. term of the 1st example. Thereby, 26g of orange oily matter is obtained.

[0106] About this oily matter, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0107] NMR;delta 8.4, 7.2 (aromatic series proton), 3.3 (methoxyl group) and 1.06 (t-butyl), IR; wave number 2845cm⁻¹ (methoxyl group), 1260 (ether), 1194, 1147 and 1094 (methoxy silyl, siloxane), GPC;MW =2500, MW/Mn =2.0.

[0108] 6-1-2. Change into a ladder siloxane according to hydrolysis, condensation, next the procedure that explained the 26g of the above-mentioned orange oily matter in the 1-1-2. term of the 1st example. Thereby, a 16g solid-state is obtained.

[0109] About this solid-state, an NMR spectrum and an IR spectrum are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0110] NMR;delta 8.4, 7.2 (aromatic series proton) and 1.06 (t-butyl), and IR; wave number [of 1260cm] - 1 (ether), 1120 (siloxane), GPC;MW =15200, and MW/Mn =8.5.

[0111] 6-1-3. Perform processing for protecting the silanol of the end of Pori (siloxane) by the trimethylsilyl radical according to the procedure explained by trimethylsilylation, next the 3-1-3.

term of the 3rd example for stabilization of a polymer to the 16g of the above-mentioned solid-states. Thereby, the resin of the 15g purpose is obtained.

[0112] About this resin, an NMR spectrum and IR SUPEKUTO are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0113] NMR;delta 8.4, 7.2 (aromatic series proton), 1.06 (t-butyl) and 0.0 (trimethyl sill radical, very minute amount), and IR; wave number [of 1260cm] - 1 (ether), 1120 (siloxane), GPC;MW =15400, and MW/Mn =1.5.

[0114] 6-2. preparation of the constituent (resist solution) of the 6th example -- mix 4ml of 2-methoxy ethyl acetate with t-butyl ester siloxane (MW =15400, MW/Mn =1.5) 0.5g of the phenol compounded as mentioned above, and triphenylsulfonium trifluoromethane sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 6th example is prepared.

[0115] 6-3. Conduct the patterning experiment at the time of using an alkali developer (however, 2.4% tetramethylammonium hydroxide water solution) to the constituent of this 6th example according to the procedure explained by the 1-3-1. term of the 1st example of a patterning experiment. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 3.5microC/cm² it is -- contrast was 5.6. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved again.

[0116] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 6th example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 5.4microC/cm² it is -- contrast was 6.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0117] 6-4. Form the pattern of the constituent of the 6th example on a lower layer with the procedure explained in the 1-4. term of the 1st example about O₂-RIE resistance, and the same procedure, and carry out oxygen plasma etching to this sample further. However, the developer uses the tetramethylammonium hydroxide water solution 2.4%.

[0118] When this plasma-etching finishing sample was observed by SEM, it turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration. in addition, the light exposure for obtaining such a pattern -- 5.0microC/cm² it was .

[0119] 7. Explain the example which made Pori (siloxane) which is the 1st component Pori (siloxane) which has C-O association of alkyl ether in a side chain as the 7th example, next the 7th example. The ether in which R4 of the above-mentioned (9) formula is shown by the above-mentioned (j) formula by this 7th example as such Pori (siloxane) (however, R2 in the (j) type uses Pori (siloxane) which is -C (CH₃).)

[0120] Processing explained in the 1-1-1. term of the 1st example is performed except using allyl compound t-butyl ether 11.6g instead of 13g of t-butyl methacrylate in the procedure of hydrosilylation explained in hydrosilylation **** of the synthetic 7-1-1. allyl compound t-butyl ether of a 7-1-t-butyl ether siloxane, and the 1-1-1. term of the 1st example. Thereby, 20g of orange oily matter is obtained.

[0121] 7-1-2. Change into a ladder siloxane according to hydrolysis, condensation, next the procedure that explained the 20g of the above-mentioned orange oily matter in the 1-1-2. term of the 1st example. Thereby, a 10g solid-state is obtained.

[0122] 7-1-3. Perform processing for protecting the silanol of the end of Pori (siloxane) by the trimethylsilyl radical according to the procedure explained by trimethylsilylation, next the 1-1-3. term of the 1st example for stabilization of a polymer to the 10g of the above-mentioned solid-states. Thereby, the resin of the 9.5g purpose is obtained.

[0123] About this resin, an NMR spectrum and IR SUPEKUTO are measured, respectively, and the determination of molecular weight is carried out by GPC. The result was as follows.

[0124] NMR;delta 1.0 (t-butyl) and 0.0 (trimethyl sill radical, very minute amount) and IR; wave number [of 1240cm] - 1 (ether), 1138 (siloxane), GPC;MW =37000, and MW/Mn =1.5.

[0125] 7-2. preparation of the constituent (resist solution) of the 6th example -- mix 4ml of 2-methoxy ethyl acetate with t-butyl ether siloxane (MW =37000, MW/Mn =1.5) 0.5g compounded as mentioned above and triphenylsulfonium trifluoromethane sulfonate 50mg. This is filtered with the membrane filter which has a hole with a diameter of 0.2 micrometers, and the constituent (resist solution) of the 7th example is prepared.

[0126] 7-3. Conduct a patterning experiment to the constituent of this 6th example according to the procedure explained by the 1-3-1. term of the 1st example except having set developing time as for 1 minute, using ethanol as a patterning experiment, next a developer. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 4.5microC/cm² it is -- contrast was 5.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved again.

[0127] Moreover, the patterning experiment at the time of using an organic solvent (a cyclohexane/dichloromethane = 2/1 mixed liquor) as a developer to the constituent of this 6th example according to the procedure explained by the 1-3-2. term of the 1st example is conducted. And sensibility, contrast, and resolution are investigated, respectively. consequently, sensibility -- 5.5microC/cm² it is -- contrast was 6.0. Moreover, it turned out that 0.4-micrometer Rhine - and - tooth space are resolved.

[0128] 7-4. Form the pattern of the constituent of the 7th example on a lower layer with the procedure explained in the 1-4. term of the 1st example about O2-RIE resistance, and the same procedure, and carry out oxygen plasma etching to this sample further. However, the developer uses ethanol.

[0129] When this plasma-etching finishing sample was observed by SEM, it turned out that Rhine - and - tooth-space pattern which are 0.4 micrometers whose thickness is about 2 micrometers are formed in the almost perpendicular configuration. in addition, the light exposure for obtaining such a pattern -- 6.0microC/cm² it was .

[0130] Although each example of the radiation sensitivity resin constituent of this invention was explained in ****, respectively, this invention is not restricted to these examples.

[0131] For example, each above-mentioned example explained the example using Pori (siloxane) which has C-O association which separates three or more carbon radicals to a side chain, and may be decomposed into it from an acid as Pori (siloxane). This is constraint from the synthetic approach of Pori (siloxane), and the purpose of this invention is attained by using as the 1st component Pori (siloxane) which has C-O association which separates one or more carbon radicals to a side chain, and may be theoretically decomposed into it from an acid.

[0132] Moreover, in each example, the frame all used the thing of ladder structure as Pori (siloxane) which has C-O association which separates one or more carbon radicals to a side chain, and may be decomposed into it from an acid. This is because silicon content is more high compared with what has a linear frame. However, even if a frame uses linear Pori (siloxane) shown, for example by the above (1), (6), or (9) formulas, the purpose of this invention is attained.

[0133] Moreover, an acid generator can acquire the same effectiveness as an above-mentioned example, also when it is made [other] suitable, such as what is shown by the suitable thing (I) except having used in the example, for example, the above-mentioned formula, - (VII).

[0134] Moreover, in the above-mentioned example, although exposed to the radiation sensitivity resin constituent concerned, using an electron ray as a radiation, the same effectiveness as an example is acquired also with the radiation of others [radiation / which is used for this exposure], such as not only an electron ray but light, an X-ray, or an ion beam.

[0135]

[Effect of the Invention] Since the acid generator of a radiation irradiation part will generate an acid and this acid will act on C-O association of the side chain of Pori (siloxane) of this radiation irradiation part further if radiations, such as light, an electron beam, an X-ray, or an ion beam, are irradiated alternatively at this according to the radiation sensitivity resin constituent of this invention so that clearly also from the explanation mentioned above, this C-O association is decomposed. Under the present circumstances, since Pori (siloxane) included in the constituent of this invention separates one or more carbon radicals to a side chain and it has the C-O association concerned, in that radiation irradiation part, a polar change produces condensation, without happening. therefore, a dissolution rate difference [as opposed to / since a difference polar in the radiation irradiation part and the non-irradiating part of a

constituent of this invention arises / the developer of both parts] -- being generated -- thereby -- high -- pattern formation [****] becomes possible.

[0136] Furthermore, with the light exposure which the light exposure at the time of exposing the radiation sensitivity resin constituent concerned may make generate a desired (the amount of catalysts) acid from an acid generator, since a polar change in Pori (siloxane) as the 1st component is produced in few acids from the acid generator as the 2nd component acting, since it will be good, the constituent concerned will become high sensitivity.

[0137] Furthermore, since Pori (siloxane) as the 1st component has silicon-oxygen association in the principal chain and it is efficiently changed into a silicon dioxide in process of processing by the oxygen plasma, dry etching resistance is also secured.

[0138] This accumulates and the radiation sensitivity resin constituent which reaches high resolution to a radiation and is excellent in O2-RIE resistance with high sensitivity again can be offered.

[0139] moreover, since the polar difference between a radiation irradiation part and a non-irradiating part is used in this way, it will obtain, if it can perform dissolving only the exposure section of the constituent after the alternative exposure of a radiation with a developer (using it as a resist of a positive type), or dissolving only an unexposed part with a developer (using it as a resist of a negative mold) to arbitration by choosing the class of developer, and an advantage is also acquired.

[0140] Moreover, in the configuration using Pori (siloxane) which has C-O association of ester in a side chain, this side chain will become a carboxylic acid if the acid from an acid generator acts. Since the acidity of a carboxylic acid is stronger than a phenol, when using for a side chain Pori (siloxane) which has C-O association of phenol alkyl ether, it can make polar change of the radiation irradiation section larger than the case where Pori (siloxane) which has C-O association of alkyl ether is used for a side chain. For this reason, when raising resolution compared with these 2 person, it is further much more advantageous.

[Translation done.]